

# Formation of zinc–zinc phosphate composite coatings by cathodic electrochemical treatment

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## Abstract

The formation of zinc–zinc phosphate composite coatings by cathodic electrochemical treatment and evaluation of its corrosion resistance is addressed in this paper. The cathodic phosphating process offers some unique advantages—it requires no specific addition of accelerator in the bath, it is capable of producing good quality coatings even at low temperature, it permits deposition of coatings of desired thickness, thus offering benefits in terms of energy savings, decrease in processing cost and improvement in plant life. Being a cathodic process, there is no iron dissolution and no ferric phosphate sludge formation, which renders it an eco-friendly process. Based on the amount of coating mass as a function of process variables and the potential-time measurement, a pictorial model is proposed for the deposition of zinc phosphate coating. The surface morphology of the coatings exhibits plate-like crystals. The corrosion behaviour of cathodically phosphated mild steel substrate in 3.5% sodium chloride solution exhibits the stability of these coatings, which last for a week with no red rust formation. This is due to the presence of a composite layer of zinc and zinc phosphate that acts as a mechanical barrier against further corrosion for a considerably longer time. Being a cathodic process, the possibility of hydrogenation of steel is the major limitation of this methodology.

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## 1. Introduction

Phosphating is the most widely used metal pretreatment process for the surface treatment and finishing of ferrous and non-ferrous metals. Due to its economy, speed of operation and ability to afford excellent corrosion resistance, wear resistance, adhesion and lubricative properties, it plays a significant role in the automobile, process and appliance industries [1–4]. Majority of the phosphating baths reported in literature require very high operating temperatures ranging from 90 to 98 °C. The main drawback associated with high temperature operation is the energy demand, which is a major crisis in the present day scenario. Besides, the use and maintenance of heating coils is difficult due to scale formation, which leads to improper heating of the bath

solution and require frequent replacement. Another problem is overheating of the bath solution, which causes an early conversion of the primary phosphate to tertiary phosphate before the metal has been treated that results in increase in the free acidity of the bath and consequently delays the precipitation of the phosphate coating [5]. One possible way of meeting the energy demand and eliminating the difficulties encountered due to scaling of heating coils and, over heating of the bath, is through the use of low temperature phosphating baths.

Though known to be in use since the 1940s [6], the low temperature phosphating processes have become more significant today due to the escalating energy costs. However, low temperature phosphating processes are very slow and need to be accelerated by some means. Acceleration of the phosphating process could be achieved by chemical, mechanical and electrochemical methods. However, each of them has some limitations and/or detrimental

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effects. Chemical accelerators are the preferred choice in many instances. The use of nitrites as the accelerator is most common in low temperature operated phosphating baths. However, a higher concentration of nitrite is required to increase the rate of deposition of phosphate coatings at low temperatures. The environmental protection agency (EPA) has classified nitrite as toxic in nature and hence use of nitrite as accelerator could cause disposal problems [7]. Though electrochemical means of acceleration has been studied earlier [8–16], the detailed information regarding the mechanism of formation and the characteristics of the coating is lacking. Though anodic means of acceleration is claimed to be more advantageous than cathodic treatment [11], the choice of a preferable method still remains ambiguous. In this context, the present paper aims to study the formation of zinc phosphate coating by cathodic electrochemical treatment.

## 2. Experimental details

The essential constituents of a zinc phosphating bath are a zinc salt, which is the source of zinc, o-phosphoric acid, a part of which reacts with the zinc salt to form soluble zinc primary phosphate and an accelerator to speed up the rate of deposition [1–5]. Besides these basic components, a variety of special additives are also added to the bath to improve the quality and performance of the resultant coatings. Since the present study focuses on the formation of zinc phosphate coating on mild steel substrates by cathodic deposition processes, the bath formulation was made using only the basic components to avoid the influence of any special additive. The composition of the baths and operating conditions used for the cathodic phosphating process is given in Table 1, which is very similar to the one used by Sinha and Feser [16] for electrochemical phosphating. The

Table 1

Chemical composition, control parameters and operating conditions of the baths used for cathodic phosphating process

	Bath A	Bath B	Bath C	Bath D	Bath E
<i>Chemical composition and operating conditions</i>					
ZnO	2.04 g/l				
H <sub>3</sub> PO <sub>4</sub> (85%)	16 ml/l				
NaOH	6.7 g/l				
Time	60 min				
Current density	4, 5 and 6 mA/cm <sup>2</sup>				
<i>Variables</i>					
pH	2.90	2.60	3.20	2.90	2.90
Temperature (°C)	27	27	27	45	60
<i>Control parameters</i>					
FA value (Points)	3.8	4.9	1.3	3.8	3.8
TA value (Points)	29.7	31.8	21.9	29.7	29.7
FA: TA	1: 7.82	1: 6.49	1: 16.85	1: 7.82	1: 7.82

FA—Free acid value; TA—Total acid value; FA:TA—Free acid to total acid ratio.

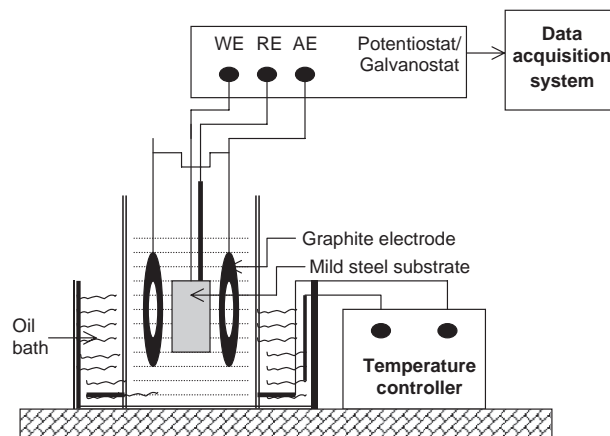


Fig. 1. The schematic of the experimental setup used for cathodic phosphating process.

bath control parameters such as free acid value (FA), total acid value (TA) and free acid to total acid ratio (FA:TA) were determined using standard procedures described elsewhere [1–5].

Mild steel substrates (composition: C: 0.16%; Si: 0.17%; Mn: 0.68%; P: 0.027%; S: 0.026%; Cr: 0.01%; Ni: 0.01%; Mo: 0.02% Fe: Balance) of 6 cm × 5 cm × 0.2 cm in size were used for the deposition of coatings by cathodic phosphating process. The oil and the greasy matter present on the substrate material, which would otherwise inhibit the coating formation, were removed by wiping with cotton soaked in trichloroethylene. The degreased panels were pickled in 10% sulphuric acid at 70–80 ° for 5–10 min to remove the rust and mill scale. The pickled panels were rinsed thoroughly in deionized water to remove the acid residues present on it after pickling. The degreased, pickled and rinsed mild steel substrates were immediately immersed into the phosphating solution contained in the beaker cell, which is maintained at the temperature required for phosphating using a constant temperature oil bath. Two sets of graphite disc electrodes (6 cm diameter) were placed on both sides of the mild steel substrate as counter electrodes. The graphite electrodes were suitably covered with a bag made of muslin cloth so that the fine graphite particles dislodged from the electrode did not contaminate the bath during deposition. The deposition of the zinc phosphate coating was carried out under galvanostatic conditions using a Potentiostat/Galvanostat (ACM Instruments, UK, Model: Gill AC). The schematic of the experimental setup is given in Fig. 1. Coating formation was allowed to proceed for 60 min after which the coated substrates were removed. The effect of process variables such as applied current density, bath pH and temperature on the amount of coating formed and the extent of metal dissolution were studied. Potential-time measurement during cathodic phosphating process was also carried out as a function of process variables such as current density, pH of the bath and temperature. The phosphated substrates were then rinsed with deionized water to remove the acid residues

and the soluble salts left after phosphating. After rinsing, the coated substrates were subjected to forced drying using a stream of compressed air.

The structural characteristic of the zinc–zinc phosphate composite coating was evaluated by X-ray diffraction measurement using Cu  $K_{\alpha}$  radiation. The surface morphology of the cathodically phosphated mild steel substrate was assessed by scanning electron microscope (SEM) (Cambridge Instruments; Model: Stereoscan 360). The corrosion resistance of the cathodically phosphated mild steel substrates in 3.5% sodium chloride solution was evaluated based on the observations made after 12 h of immersion for the discolouration of the solution and rusting of the panels and the loss in mass measured after 24 h of immersion.

### 3. Results and discussion

#### 3.1. Effect of process variables on coating mass

Coating mass is the prime factor widely used in industries to assess the quality of a phosphating bath and is strongly recommended by many specifications [17,18]. Further, based on the coating mass values, phosphate coatings have been classified into different categories and recommended for different end uses.

Current density is one of the major factors that influence the extent of phosphate coating formation. During cathodic phosphating, the applied current density is initially varied between 1 and 8 mA/cm<sup>2</sup> and the deposition was carried out using bath A for 1 h. The effect of current density on phosphate coating mass is shown in Fig. 2. It is evident from Fig. 2 that the coating mass increases with increase in current density and reaches a maximum at 6 mA/cm<sup>2</sup>, beyond which there observed to be saturation in coating mass. Increase in current density is expected to accelerate the rate of coating formation and this effect is pronounced up to 6 mA/cm<sup>2</sup>. The saturation

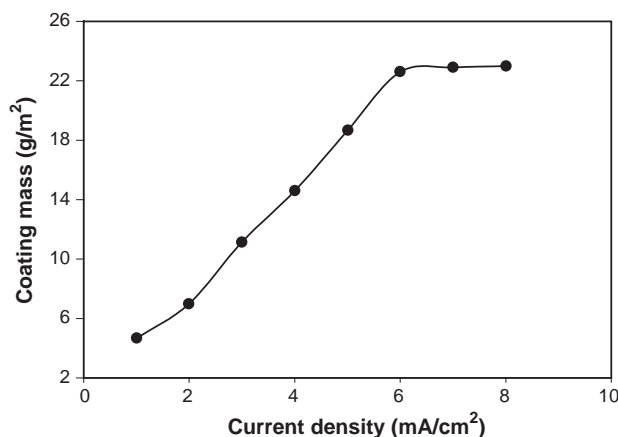


Fig. 2. Effect of applied current density (1–8 mA/cm<sup>2</sup>) on phosphate coating mass obtained using bath A by cathodic phosphating (pH 2.9; Temperature: 27 °C; Time: 60 min.).

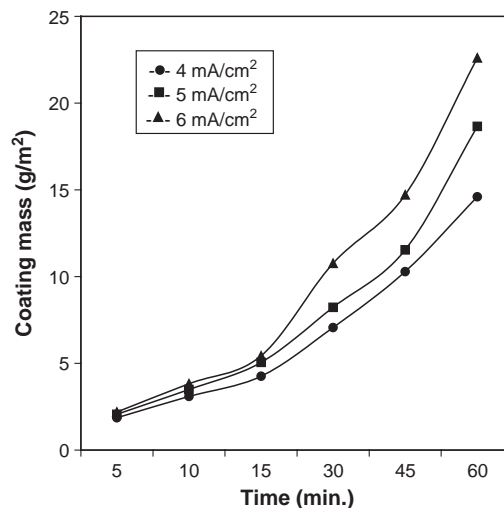


Fig. 3. Effect of applied current density (4–6 mA/cm<sup>2</sup>) on phosphate coating mass obtained using bath A by cathodic phosphating (pH: 2.9; Temperature: 27 °C).

in coating mass beyond 6 mA/cm<sup>2</sup> might either be due to the spalling of the coating during deposition or change in interfacial pH that would affect the deposition of zinc phosphate. Hence based on the amount of coating formed and uniformity, further studies were carried out in the current density range of 4–6 mA/cm<sup>2</sup>.

##### 3.1.1. Effect of current density on coating mass

The effect of applied current density (4–6 mA/cm<sup>2</sup>) on phosphate coating mass vs. exposure time obtained using bath A is shown in Fig. 3. Obviously, the amount of coating formed increases with increase in current density as well as the time of deposition. A similar trend is also observed when the pH of the bath is varied to 2.60 (bath B) and 3.20 (bath C).

##### 3.1.2. Effect of bath pH on coating mass

The effect of pH (2.60, 2.90 and 3.20) on phosphate coating mass vs. exposure time obtained using baths A, B and C at 4 mA/cm<sup>2</sup> is shown in Fig. 4. Increase in bath pH leads to an increase in coating mass. This trend is also observed at 5 and 6 mA/cm<sup>2</sup>.

##### 3.1.3. Effect of temperature on coating mass

The effect of temperature (27, 45 and 60 °C) on phosphate coating mass vs. exposure time obtained using baths A, D and E, at 4 mA/cm<sup>2</sup> is shown in Fig. 5. Increase in temperature leads to an increase in coating mass. This trend is also observed at 5 and 6 mA/cm<sup>2</sup>.

During cathodic phosphating, hydrogen evolution occurs at the cathode (mild steel substrate), which causes a rise in interfacial pH. Following this, the soluble primary phosphate is converted into insoluble tertiary phosphate [point of incipient precipitation (PIP)] and deposited on the mild steel substrate. The rate of hydrogen evolution and extent of rise in interfacial pH determine the amount of phosphate coating

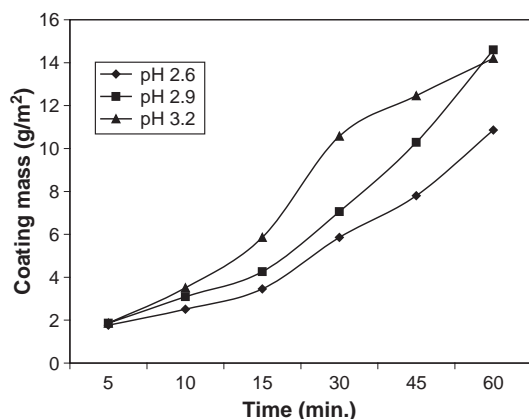
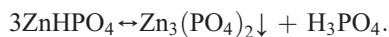
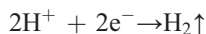


Fig. 4. Effect of bath pH on phosphate coating mass obtained by cathodic phosphating (current density: 4 mA/cm<sup>2</sup>; temperature: 27 °C).

formed. The increase in coating mass with increase in current density, increase in bath pH and increase in temperature is due to the earlier attainment of PIP.



Hence it is evident that the deposition of zinc phosphate coating on mild steel surface is a function of interfacial pH, which is influenced by the current density, pH and temperature. However, during cathodic electrochemical treatment, besides zinc phosphate, zinc is also deposited on the mild steel substrate. As a result, the interfacial pH will decrease and this might inhibit the deposition of zinc phosphate. At higher current densities the extent of zinc deposition is high and the extent of decrease in interfacial pH is also high. In fact this is the reason for the observed saturation in the coating mass beyond 6 mA/cm<sup>2</sup> (Fig. 2).

The coating mass values suggest only the amount of coating formed and do not provide any information regarding the kinetics of coating formation. Much informa-

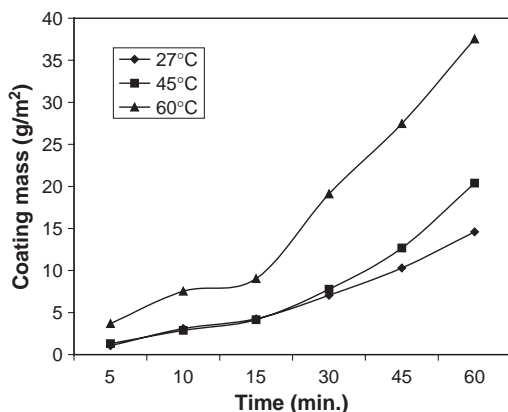


Fig. 5. Effect of bath temperature on phosphate coating mass obtained by cathodic phosphating (pH: 2.9; current density: 4 mA/cm<sup>2</sup>).

tion on the kinetics and mechanism of the phosphating process can be inferred from potential-time measurements rather than the coating mass measurements. Literature reports reveal that the kinetics of phosphate coating formation is best followed by measuring the changes in potential of the substrate as a function of time (potential-time measurements) [19–23].

### 3.2. Potential-time measurements

During cathodic phosphating, the potential of the substrate is monitored continuously as a function of time for the entire duration of coating deposition. The potential-time curves obtained for all the baths exhibit a similar trend. The potential-time curve recorded during cathodic electrochemical treatment using bath B at 5 mA/cm<sup>2</sup> for 1 h is shown in Fig. 6 as a model curve. The potential-time curves of the present study could be analyzed by dividing them in to three segments as follows:

Segment I—Change in potential from initial to maximum value,

Segment II—Change in potential from maximum to initial stabilization point,

Segment III—Change in potential after initial stabilization point.

#### 3.2.1. Segment I

The change in potential from initial to maximum value is indicative of the nature of the metal surface during the initial stages of coating formation. In this segment, the potential of the mild steel substrate is shifted towards more cathodic direction. Shift in potential towards cathodic direction during the initial stages of coating formation is also observed in conventional phosphating process due to the corrosive attack by the free phosphoric acid present in the bath [19–23]. The extent of shift in potential in conventional phosphating process is moderate (about 50–100 mV)

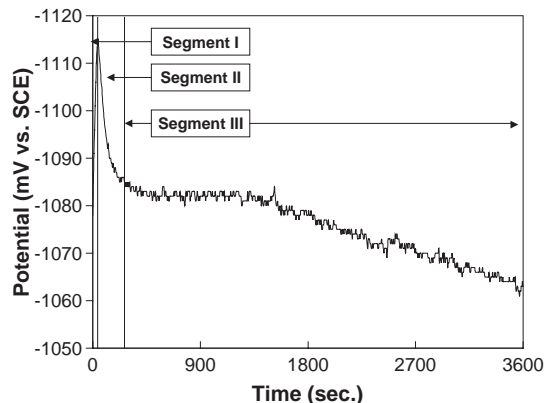
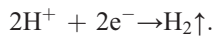
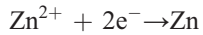


Fig. 6. Potential-time curve recorded during cathodic electrochemical treatment using bath B at 5 mA/cm<sup>2</sup> for 1 h depicting the classification of three different segments of the curve to analyze the changes that occur during cathodic phosphating process.

and the potential of the substrate is found to be around  $-520$  mV, which is the characteristic potential of mild steel in zinc phosphating bath [21–23]. However, in cathodic phosphating, the extent of shift in potential is very high of the order of  $500$ – $700$  mV and the potential of the substrate is around  $-1200$  mV, which could not be accounted for a mere attack by the free phosphoric acid. Considering the bath composition and operating conditions, one possible reason for such a large shift in potential is the deposition of zinc accompanied by hydrogen evolution as follows:



The very high applied cathodic current strongly suggests such a possibility. This is further confirmed by chemical analysis of coating deposited during this segment that reveals the absence of phosphorus and presence of zinc. Hence it is evident that deposition of zinc is the predominant reaction during the first segment.

The extent of shift in potential observed in this segment is due to the competition between zinc deposition and hydrogen evolution, which is a function of process variables, such as current density, pH of the bath and temperature. Increase in current density, increase in bath pH and temperature results in pronounced shift in potential towards more negative values, indicating predominant zinc deposition under these conditions (Fig. 7(a–c)).

### 3.2.2. Segment II

This segment represents the change in potential from maximum value towards anodic direction (less negative values) until a stabilization point is reached. Shift in potential towards anodic direction is also observed in conventional phosphating process, which can be accounted for the deposition of zinc phosphate coating [19–23]. Hence the shift in potential observed in this segment is due to the deposition of zinc phosphate coating on the substrate. The maximum potential (starting point of segment II) represents the onset of conversion of soluble primary phosphate to insoluble tertiary phosphate (point of incipient precipitation), following the rise in interfacial pH. Further anodic shift in potential represents the progressive buildup of the phosphate coating formation. The extent of shift in potential towards anodic direction is of the order of only  $50$  mV, which suggests that the codeposition of zinc might also occur during this segment. However, the predominant reaction during this segment is the deposition of zinc phosphate coating. The stabilization in potential value noted at the end of segment II is due to the sudden decrease in the rate of conversion of primary phosphate to tertiary phosphate as well as zinc deposition and hydrogen evolution. This behaviour is due to the delayed attainment of rise in interfacial pH, which in turn is decided by the available metallic surface sites for coating formation, which reaches almost a constant value at this stage.

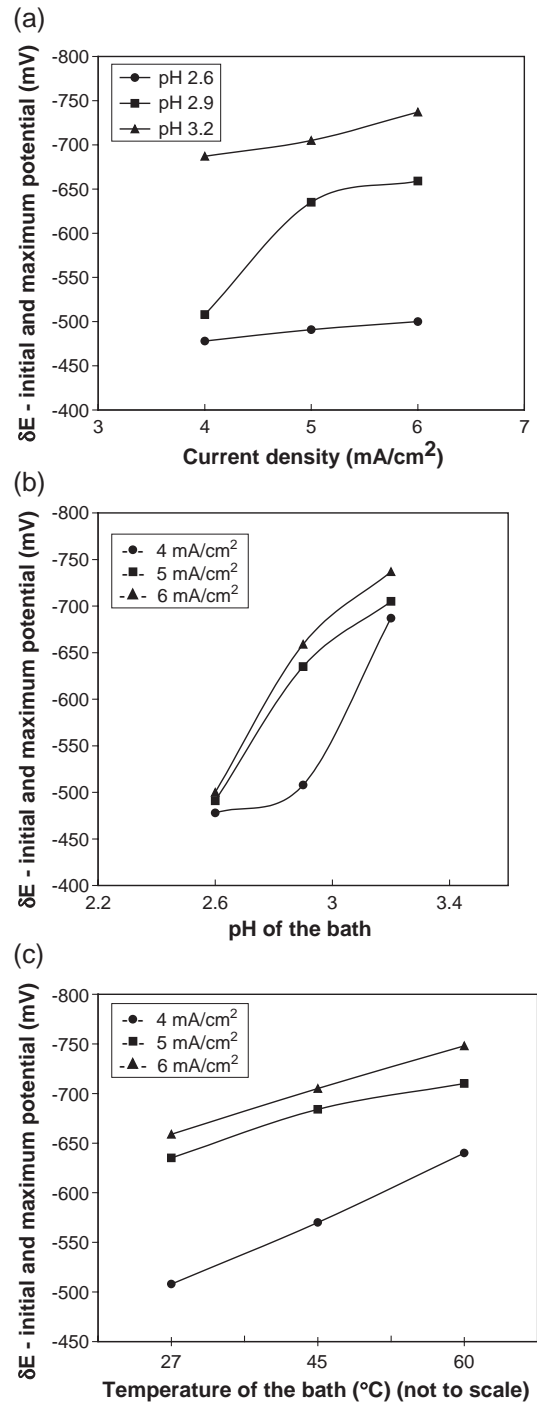


Fig. 7. Extent of change in potential between the initial and maximum potential as a function of (a) current density; (b) pH of the bath; and (c) bath temperature.

The extent of shift in potential observed in this segment is due to the competition among hydrogen evolution and deposition of zinc and zinc phosphate, which is a function of process variables, such as current density, pH of the bath and temperature. Increase in current density results in a smaller shift in potential towards cathodic direction (Fig. 8(a)). This can be attributed to the favourable condition for zinc deposition with increase in current density. Contrarily,



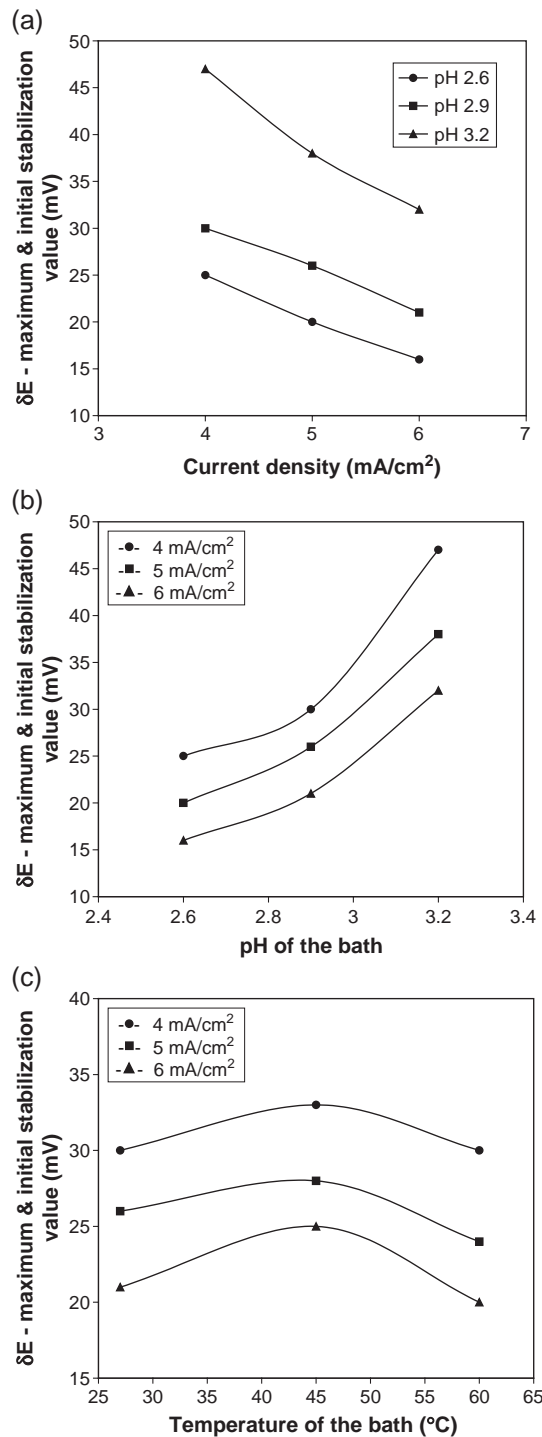


Fig. 8. Extent of change in potential between the maximum and initial stabilization point as a function of (a) current density; (b) pH of the bath; and (c) bath temperature.

increase in pH causes a pronounced shift in potential towards cathodic direction (Fig. 8(b)). This can be attributed to the earlier attainment of PIP and favourable condition for zinc phosphate deposition. Increase in temperature favours the diffusion of both  $\text{Zn}^{2+}$  and  $\text{H}^{+}$  ions to get reduced at the substrate as well as promote an earlier attainment of PIP. Hence the magnitude of potential shift is moderate (Fig. 8(c)).

### 3.2.3. Segment III

This segment represents the change in potential between the initial stabilization point and the end of the deposition period and also covers a larger portion of the potential-time curve. Codeposition of zinc and zinc phosphate occurs in this segment. Process variables, such as current density, pH

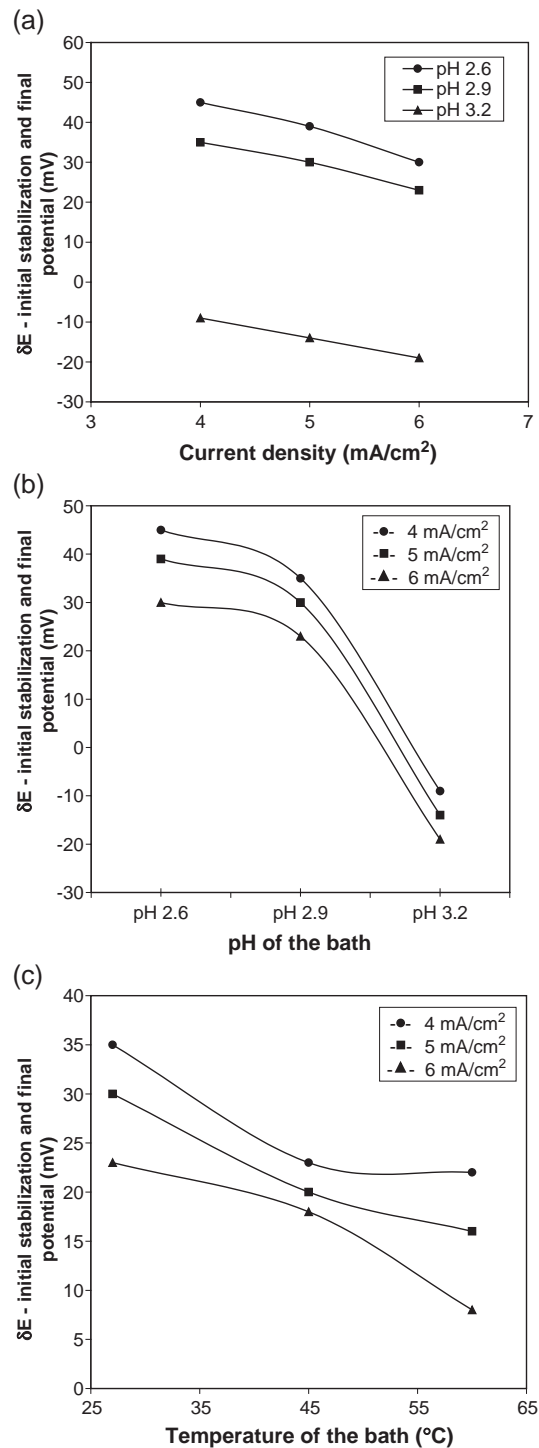


Fig. 9. Extent of change in potential between the initial stabilization point and the final potential as a function of (a) current density; (b) pH of the bath; and (c) bath temperature.

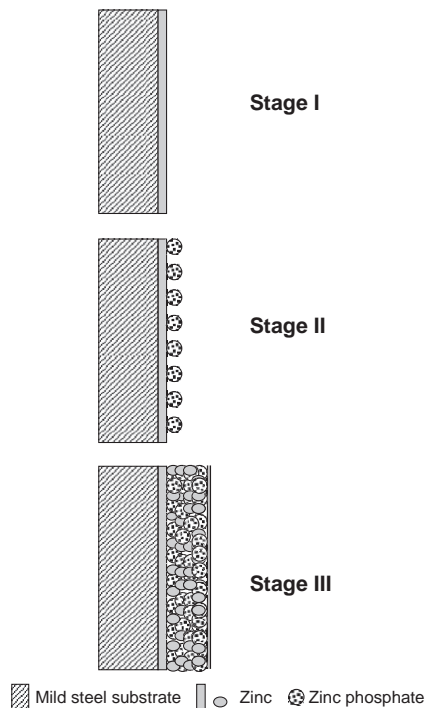


Fig. 10. Pictorial model depicting the three stages of coating formation during cathodic phosphating process.

and temperature of the bath determine the ratio of zinc to zinc phosphate in the coating. Conditions that favour zinc deposition result in shift in potential towards the cathodic direction (Fig. 9(a) and (b)) whereas conditions favouring phosphate deposition result in a shift in potential towards the anodic direction (Fig. 9(c)).

### 3.3. Mechanism of coating formation

Coating mass measurements suggest that the increase in coating mass with increase in current density, increase in bath pH and increase in temperature is due to the earlier attainment of PIP. Potential-time measurements suggest the formation of zinc coating during the initial periods, followed by the codeposition of zinc and zinc phosphate in subsequent stages. The ratio of zinc to zinc phosphate is very high during stage I, decreased in stage II and stabilizes almost to a constant value in stage III. Hence it can be visualized that during stage I, a thin layer of zinc deposits on the entire surface of the mild steel substrate with a simultaneous hydrogen evolution. The consumption of available  $H^+$  ions at the metal-solution interface results in a progressive rise in the interfacial pH and favours the conversion of soluble primary phosphate to insoluble tertiary phosphate. As a result, the zinc phosphate coating deposits on the substrate, which is already coated with a thin layer of zinc. The continued deposition of zinc and hydrogen evolution reaction enables further deposition of zinc phosphate on adjacent areas. The available metallic sites (zinc) decrease with the progress in coating formation and reach almost a constant value. The continuous evolution of hydrogen visually observed throughout the entire duration of deposition suggests the availability of metallic site (zinc) at the surface at any given time. It is presumed that the deposition of zinc proceeds in the form of fixed channels surrounded by zinc phosphate throughout the thickness of the coating. In conventional phosphating, the interfacial rise in pH is controlled by the diffusion of  $H^+$  ions through the pores, which limits the amount of coating

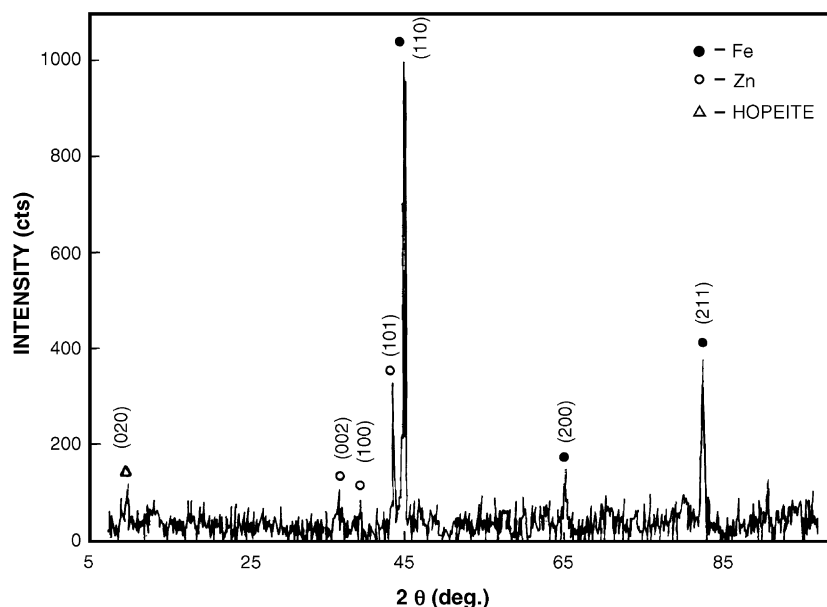


Fig. 11. X-ray diffraction pattern of zinc–zinc phosphate composite coating prepared using bath A at 6 mA/cm<sup>2</sup>.

formation, whereas in cathodic phosphating, the coating formation could be extended continuously to build thick deposits up to  $60 \text{ g/m}^2$  (in case of bath A at  $60^\circ\text{C}$ ). Based on the above findings, a pictorial model for the mechanism of coating formation during cathodic phosphating is proposed (Fig. 10).

Being a cathodic process, the possibility of hydrogenation of steel is not ruled out. It is particularly crucial if the substrate used is high-carbon or high-alloy, hardened, high strength steels. In fact, this is the major limitation of this methodology of preparing zinc–zinc phosphate composite coating. It is recommended to perform an embrittlement relief heat-treatment after deposition of the zinc–zinc phosphate composite coating, which would otherwise affect the mechanical properties of the steel. The exact temperature and time of relief heat-treatment depend on the tensile strength/hardness of the steel used for the deposition of the composite coating. A conventional callout for hydrogen relief heat-treatment is  $200^\circ\text{C}$  for 3 h, within 4 h of deposition of the coating. If the substrate/component is subject to flexure or extreme loading, the baking time may be extended to 8 or even 24 h, depending on the requirements.

The colour of the zinc–zinc phosphate composite coating obtained by cathodic phosphating process remains as gray with bright crystalline luster and is highly uniform. Adhesion of the phosphate coating on the mild steel substrate evaluated by pull-off test with a pressure sensitive adhesive tape is found to be good and is highly comparable with the adhesion of the zinc phosphate coating on steel substrate prepared by conventional chemical phosphating technique. The coatings obtained with the cathodic phosphating process are expected to be rich in hopeite phase ( $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ) with elemental zinc and mostly free from phosphophyllite phase ( $\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ). X-ray diffraction measurement performed on zinc–zinc phosphate composite coated mild steel substrate confirms the presence of zinc and hopeite phase (Fig. 11). The surface morphology of cathodically phosphated mild steel substrates assessed by scanning electron microscope (SEM) is shown in Fig. 12(a–c). The formation of plate-or-flower like crystals is characteristic of the hopeite phase ( $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ). The crystallite size of the coating increases with increase in current density. For coatings prepared at  $6 \text{ mA/cm}^2$ , where the zinc content of the coating is high, the morphology of the coating resembles that of electrodeposited zinc [24].

### 3.4. Evaluation of corrosion performance

Immersion in 3.5% NaCl solution provides an insight into the corrosion behaviour of phosphated mild steel substrates. The extent of corrosion is assessed by visual observation after 12 h of immersion and by measuring the loss in mass due to corrosion after 24 h of immersion. Observations made after 12 h (Table 2) reveal that the cathodically phosphated mild steel substrates remain in

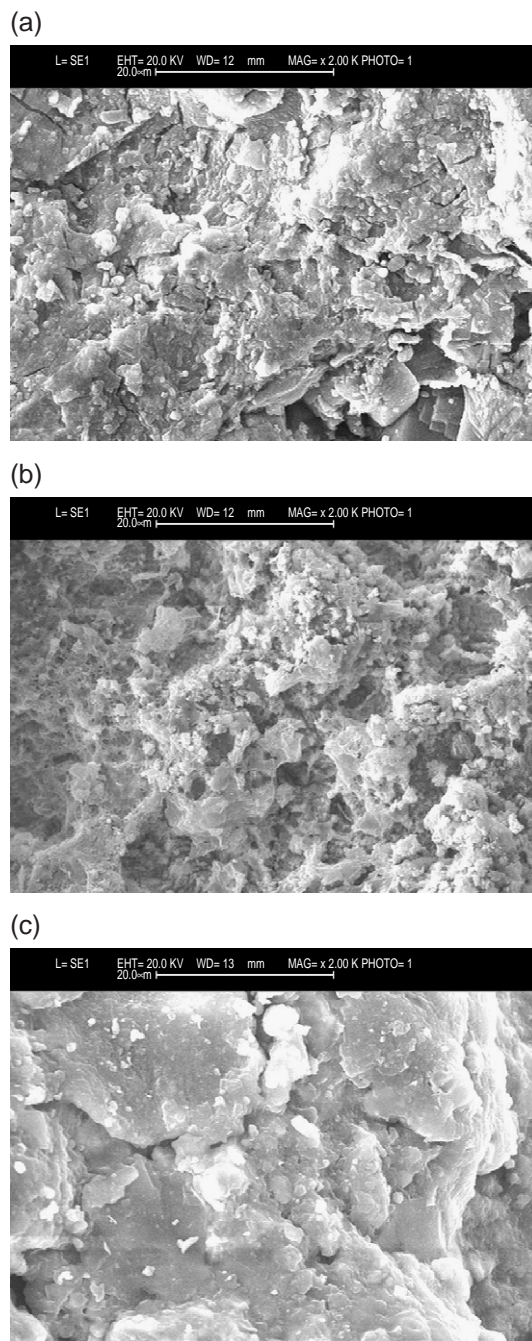


Fig. 12. Surface morphology of the cathodically phosphated mild steel substrates using bath A at different current densities (a)  $4 \text{ mA/cm}^2$ ; (b)  $5 \text{ mA/cm}^2$ ; and (c)  $6 \text{ mA/cm}^2$ .

good condition and show no red rust formation. However, discolouration of the solution occurs in the case of uncoated mild steel substrate, indicating a higher amount of iron dissolution. The appearance of a yellowish orange precipitate of ferric hydroxide following the hydrolysis of iron (II) chloride formed by the attack of chloride ions at the uncoated areas indicate greater corrosion and discolouration of the solution in the case of uncoated steel. The absence of red rust on the surface of phosphated steel indicates that cathodically phosphated mild steel substrates



Table 2

Corrosion resistance of cathodically phosphated mild steel substrate subjected to immersion in 3.5% sodium chloride solution for 24 h

System studied	Observations after 12 h	Mass loss (g/m <sup>2</sup> ) after 24 h
Uncoated mild steel	Discolouration of the solution Red rust formation on the surface of the substrate	24.2
Mild steel substrate cathodically phosphated at 4 mA/cm <sup>2</sup>	No discolouration of the solution No red rust formation on the surface of the substrate	1.7
Mild steel substrate cathodically phosphated at 5 mA/cm <sup>2</sup>	No discolouration of the solution, no red rust formation on the surface of the substrate	1.4
Mild steel substrate cathodically phosphated at 6 mA/cm <sup>2</sup>	No discolouration of the solution, no red rust formation on the surface of the substrate	1.3

are more uniform and possess a good corrosion resistance. One interesting observation with the cathodically phosphated mild steel is the formation of zinc based corrosion product (white rust) on the surface of the coating. A small quantity of it is also observed in the bulk solution due to spalling of the corrosion products. The white rust is formed as a result of the dissolution of zinc present in cathodically phosphated steel by sacrificial effect and deposits on the surface, which in turn improves the protective ability of the coating. Following this, the corrosion resistance of cathodically phosphated mild steel substrate is considerably improved. The improvement in corrosion resistance compared to uncoated mild steel substrate is also reflected in the loss in mass due to corrosion measured after 24 h (Table 2).

#### 4. Conclusions

The baths used for cathodic phosphating process contain only the essential constituents and require no specific addition of accelerator in the bath. These baths are capable of producing good quality coatings even at low temperature. Moreover, they permit to build coatings of desired thickness (higher coating mass). This ability offers benefits in terms of energy savings, decrease in processing cost and improvement in plant life. Being a cathodic process, there is no iron dissolution and hence no ferric phosphate sludge formation in the bath. This attribute renders the cathodic phosphating process eco-friendly. The phosphate coating mass increases with increase in current density, bath pH and temperature (in the ranges studied), due to the earlier attainment of PIP. Potential time measurements indicate that the coating formation proceeds through three stages, in which deposition of zinc, deposition of zinc phosphate and codeposition of zinc and zinc phosphate, respectively, are the predominant reactions in these three stages. The mechanism of coating formation in the cathodic phosphating process involves mainly proton reduction (hydrogen evolution) and the associated counter-phenomenon viz., zinc deposition, in the first stage followed by the predominant zinc phosphate deposition in the second stage. The competition between deposition of zinc and that of zinc phosphate continues until an equilibrium is established, after which they proceed with

almost equal rates. The surface morphology of the coatings obtained by cathodic phosphating process exhibits plate-like crystals. The corrosion behaviour of cathodically phosphated mild steel substrate in 3.5% sodium chloride solution exhibits the stability of these coatings, which last for a week's time with no red rust formation. This is due to the presence of a composite layer of zinc and zinc phosphate that acts as a mechanical barrier against further corrosion for a considerably longer time. Being a cathodic process, the possibility of hydrogenation of steel is the major limitation of this methodology.

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